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(54) Title: CEMENT ADMIXTURE AND CEMENT COMPOSITION

(57) Abstract: It is an object of the present invention to provide a cement admixture capable of exhibiting high cement dispersing ability at low addition levels, in particular capable of displaying excellent initial dispersing ability and dispersion retaining ability even in a high water reducing ratio range, and a cement composition in which this admixture is used. A cement admixture comprising two polymers, namely a polymer (A) and a polymer (B), as essential constituents in a ratio of polymer (A) to polymer (B) between 1 to 99/99 to 1% by mass, wherein the polymer (A) is a polymer comprising, as essential constituent units, a constituent unit (I) derived from an unsaturated (poly)alkylene glycol ether monomer (a) and a constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b) and wherein the constituent units (I) and (II) each ac-counts for not less than 1% by mass relative to all constituent units but the constituent unit (I) accounts for not more than 50 mole percent relative to all constituent units and, wherein the polymer (B) is an oxyalkylene group- or polyoxyalkylene group- and carboxyl group-containing polymer.

CEMENT ADMIXTURE AND CEMENT COMPOSITION

BACKGROUND OF THE INVENTION

The present invention relates to a cement admixture and a cement composition comprising the same.

Prior Art

A cement paste prepared by adding water to cement, a mortar prepared by admixing sand, which is a fine aggregate, therewith, and a concrete prepared by further admixing gravel, which is a coarse aggregate, therewith are used in large amounts in various structural materials and the like. However, with the lapse of time, mortar and concrete harden because of the progress of the hydration reaction between cement and water and, therefore, their workability generally decreases with the time after addition of water. For securing the dispersing ability of such cement, various cement admixtures have been developed.

Thus, for example, Japanese Kokoku Publication Sho-59-18338 discloses a cement dispersant produced by copolymerization of a polyalkylene glycol mono(meth)acrylate ester monomer and a (meth)acrylic acid monomer. The cement dispersant disclosed in the cited patent specification has polyalkylene glycol chains, which are nonionic hydrophilic groups, and anionic carboxyl groups in each molecule and the hydrophilicity and steric hindrance of the former inhibit the adsorption of the latter to cement particles and, allegedly, its setting retarding effect is weak and its dispersing performance is good.

Japanese Kokai Publication Hei-04-175254 discloses a cement dispersant comprising two kinds of polymer, wherein the first component is a polyether compound derived from a copolymer of maleic anhydride and a polyalkylene glycol allyl alkyl ether by further monoesterification with

alkylpolyalkylene glycol and the second component is a salt of a polycarboxylic acid, which is a polymer of (meth)acrylic acid or the like. Allegedly, the second component polycarboxylic acid salt incorporated in the cement dispersant disclosed in the above-cited patent specification is first preferentially adsorbed on cement particles and disperses the cement particles in water and, then, the polyether compound contained as the first component and slow in rate of adsorption on cement particles is adsorbed on cement, whereby the dispersing ability of cement can be secured for a long period of time.

Japanese Kokai Publication Hei-05-345647 also discloses cement dispersant comprising two kinds of polymer, wherein the first component is a copolymer (a) of maleic anhydride and alkenyl ether with not less than 100 moles of an oxyalkylene group added and the second component is polycarboxylic acid type cement dispersant (b). It is described in the cited patent specification that the component (b) serves to increase the dispersing ability of cement at an early stage and the component (a), in which the number of moles of the oxyalkylene group added is not less than 100, causes a hydrated layer to be formed around each polyoxyalkylene group extending from the copolymer adsorbed on cement particles and, owing to the resulting steric hindrance, the dispersing ability of cement particles is retained for a prolonged period of time and that an increase in polyether chain length in component (a) results in a tendency to increase the slump with time.

Japanese Kokai Publication Hei-07-267705 discloses a cement dispersant comprising three kinds of polymer, in which the first component is a copolymer (a) of a polyalkylene glycol mono(meth)acrylate compound and a (meth)acrylic acid compound, the second component is a copolymer (b) of a polyalkylene glycol mono(meth)allyl ether compound and maleic anhydride and the third component

is a copolymer (c) of a polyalkylene glycol mono(meth)allyl ether compound and a maleic acid-esterified polyalkylene glycol compound. The cited patent specification describes that the component (a), when used alone, increases the initial flowability of cement but is poor in slump-retaining ability and increases the viscosity of the cement composition, that the component (b), when used alone, requires time to increase the initial flowability and, even when the initial flowability is increased by increasing the level of addition thereof, it causes phase separation of the cement composition with time, that the component (c), when used alone, is further poor in cement dispersing ability and that, therefore, such effects that cannot be obtained by the single use of each of the three components are produced by combinedly using them in specific proportions. Thus, it is presumed, in the cited specification, that the differences in mechanisms of action on cement among the components are due to the molecular structures of the components and the differences in initial flowability increasing effect are due to the higher rate of adsorption, on cement particles, of the (meth)acrylic acid-based functional group-containing polymer (component a) as compared with the maleic acid-based functional group-containing polymers (components b and c). It is further described that the component higher in rate of adsorption is poor in the ability to subsequently retain the flowability.

Further, Japanese Kokai Publication 2001-19514 also discloses a cement dispersant comprising two kinds of polymer, wherein the first component is a polymer (A) of a polyalkylene glycol mono(meth)acrylate monomer and a (meth)acrylic acid monomer and the second component is a polymer (B) of a polyalkylene glycol monoalkenyl ether and maleic acid. The cited patent specification describes that when the carboxyl group content and the addition number of

moles of the alkylene oxide to attain the polyalkylene glycol chain length in these polymers are within respective specific ranges, the combined use of the polymers can provide such excellent initial dispersing ability and slump-retaining ability that cannot be attained with the conventional products.

Japanese Kokai Publication 2001-34151 also discloses a cement admixture comprising two species of copolymers obtained by copolymerization of two or more species of unsaturated (poly)alkylene glycol ether monomers having a specific structure and (meth)acrylic acid monomers. In Example, an unsaturated (poly)alkylene glycol ether monomer which contains a terminal alkyl group containing 1 to 3 carbon atoms and a short (poly)alkylene glycol chain, is used. When the unsaturated (poly)alkylene glycol ether monomer contains an alkyl group as a terminal group and a short (poly)alkylene glycol chain for increasing shrinkage decreasing effects of concrete, its hydrophobicity increases to thereby reduce the dispersing ability of copolymers. In particular, there are no dispersants available for providing cement with sufficient dispersing ability in a high water reducing ratio range.

Thus, the technique is known in the art which comprises incorporating a polyalkylene glycol mono(meth)acrylate/(meth)acrylic acid copolymer and a polyalkylene glycol monoalkenyl ether/maleic acid copolymer combinedly in cement admixtures. At present, however, it is impossible to secure both sufficient initial dispersing ability and dispersion retaining ability with each other; for the manifestation of sufficient initial dispersing ability, it is necessary to add the dispersants in large amounts. In particular, there are no dispersants available for providing cement with sufficient dispersing ability and dispersion retaining ability in a high water reducing ratio range.

In view of the above-mentioned state of the art, it is an object of the present invention to provide a cement admixture capable of exhibiting high cement dispersing ability at low addition levels, in particular capable of displaying excellent initial dispersing ability and dispersion retaining ability even in a high water reducing ratio range, and a cement composition in which this admixture is used.

SUMMARY OF THE INVENTION

As a result of intensive investigations, the present inventors found that a mixture comprising a combination of a specific (poly)alkylene glycol alkenyl ether compound obtained by using an unsaturated monocarboxylic acid monomer as an essential comonomer constituent in lieu of maleic acid that has so far been used, and a (poly)oxyalkylene group- and carboxyl group-containing compound can show excellent initial dispersing ability and dispersion retaining ability even in a high water reducing ratio range. They further found that a mixture comprising a combination of a (poly)oxyalkylene group- and carboxyl group-containing compound and a specific (poly)alkylene glycol alkenyl ether compound obtained by using an unsaturated monocarboxylic acid ester monomer as an essential comonomer constituent can exhibit excellent dispersion retaining ability with time even in a high water reducing ratio range. These and other findings have now led to completion of the present invention. In the following, the invention is described in detail.

The present invention includes the following 1) to 14) aspects:

1) A cement admixture comprising

two polymers, namely a polymer (A1) and a polymer (B1), as essential constituents in a ratio of polymer (A1) to polymer (B1) between 1 to 99/99 to 1% by mass,

wherein the polymer (A1) is a polymer comprising, as essential constituent units, a constituent unit (I) derived from an unsaturated (poly)alkylene glycol ether monomer (a1) represented by the general formula (1):

$YO(R^1O)_mH$ (1)

wherein Y represents an alkenyl group containing 2 to 8 carbon atoms, the m R^1O groups are the same or different and each R^1O represents an oxyalkylene group containing 2 to 18 carbon atoms and m is a mean addition number of moles of the oxyalkylene group and represents a number of 1 to 500,

and a constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b) and

wherein the constituent units (I) and (II) each accounts for not less than 1% by mass relative to all constituent units but the constituent unit (I) accounts for not more than 50 mole percent relative to all constituent units and,

wherein the polymer (B1) is an oxyalkylene group- or polyoxyalkylene group- and carboxyl group-containing polymer.

2) A cement admixture comprising

two polymers, namely a polymer (A2) and a polymer (B2), as essential constituents in a ratio of polymer (A2) to polymer (B2) between 1 to 99/99 to 1% by mass,

wherein the polymer (A2) is a polymer comprising, as essential constituent units, a constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the general formula (2):

$YO(R^1O)_nR^2$ (2)

wherein Y represents an alkenyl group containing 2 to 8 carbon atoms, the n R^1O groups are the same or different and each R^1O represents an oxyalkylene group containing 2 to 18 carbon atoms, R^2 represents a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms and n is

a mean addition number of moles of the oxyalkylene group and represents a number of 1 to 500,

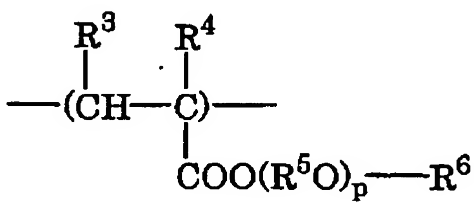
a constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b) and a constituent unit (III) derived from an unsaturated monocarboxylic ester monomer (c),

wherein the constituent units (I'), (II) and (III) each accounts for not less than 1% by mass relative to all constituent units but the constituent unit (I') accounts for not more than 50 mole percent relative to all constituent units and the sum of the proportions of the constituent units (II) and (III) is greater than the proportion of the constituent unit (I') on the mole ratio basis,

wherein the polymer (B2) is an oxyalkylene group- or polyoxyalkylene group- and carboxyl group-containing polymer.

3) The cement admixture according to (2),

wherein the constituent unit (III) derived from an unsaturated monocarboxylic acid ester monomer (c) is a constituent unit (IV) derived from a (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d) represented by the general formula (3):

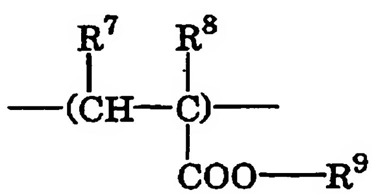


(3)

wherein R^3 and R^4 are the same or different and each represents a hydrogen atom or a methyl group, the p R^5O groups are the same or different and each R^5O represent an oxyalkylene group containing 2 to 18 carbon atoms, p is a

mean addition number of moles of the oxyalkylene group and represents a number of 1 to 500, and R^6 represents a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms,

or a constituent unit (VI) derived from a hydrophobic unsaturated monocarboxylic acid ester monomer (f) represented by the general formula (4):



(4)

wherein R^7 and R^8 are the same or different and each represents a hydrogen atom or a methyl group and R^9 represents a hydrocarbon group containing 1 to 30 carbon atoms.

4) A cement admixture comprising

two polymers, namely a polymer (A3) and a polymer (B3), as essential constituents in a ratio of polymer (A3) to polymer (B3) between 1 to 99/99 to 1% by mass,

wherein the polymer (A3) is a polymer comprising, as essential constituent units, a constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the general formula (2):

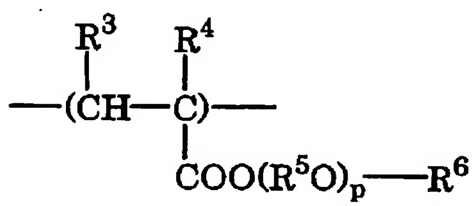
$YO(R^1O)_nR^2$ (2)

wherein Y represents an alkenyl group containing 2 to 8 carbon atoms, the n R^1O groups are the same or different and each R^1O represents an oxyalkylene group containing 2 to 18 carbon atoms, R^2 represents a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms and n is a mean addition number of moles of the oxyalkylene group and represents a number of 1 to 500,

and a constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b) and

wherein the constituent units (I′) and (II) each accounts for not less than 1% by mass relative to all constituent units but the constituent unit (I′) accounts for not more than 50 mole percent relative to all constituent units and

wherein the polymer (B3) is a polymer comprising a constituent unit (IV) derived from a (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d) represented by the general formula (3):



(3)

wherein R^3 and R^4 are the same or different and each represents a hydrogen atom or a methyl group, the p R^5O groups are the same or different and each R^5O represent an oxyalkylene group containing 2 to 18 carbon atoms, p is a mean addition number of moles of the oxyalkylene group and represents a number of 1 to 500, and R^6 represents a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms,

and a constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b).

5.) A cement admixture comprising

two polymers, namely a polymer (A3) and a polymer (B4), as essential constituents in a ratio of polymer (A3) to polymer (B4) between 1 to 99/99 to 1% by mass,

wherein the polymer (A3) is a polymer comprising, as essential constituent units, a constituent unit (I′)

derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the general formula (2):

$YO(R^1O)_nR^2$ (2)

wherein Y represents an alkenyl group containing 2 to 8 carbon atoms, the n R^1O groups are the same or different and each R^1O represents an oxyalkylene group containing 2 to 18 carbon atoms, R^2 represents a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms and n is a mean addition number of moles of the oxyalkylene group and represents a number of 1 to 500,

and a constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b),

wherein the constituent units (I') and (II) each accounts for not less than 1% by mass relative to all constituent units but the constituent unit (I') accounts for not more than 50 mole percent relative to all constituent units,

wherein the polymer (B4) is a polymer comprising a constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the general formula (2) and a constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e).

6) A cement admixture comprising two polymers, namely a polymer (G) and a polymer (B5), as essential constituents in a ratio of polymer (G) to polymer (B5) between 1 to 99/99 to 1% by mass,

wherein the polymer (B5) is an oxyalkylene or polyoxyalkylene group- and carboxyl group-containing polymer and

the polymer (G) is a polymer comprising, as essential constituent units, a constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the general formula (2):

$YO(R^1O)_nR^2$ (2)

wherein Y represents an alkenyl group containing 2 to 8

carbon atoms, the n R^1O groups are the same or different and each R^1O represents an oxyalkylene group containing 2 to 18 carbon atoms, R^2 represents a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms and n is the mean addition number of moles of the oxyalkylene group and represents a number of 1 to 500,

and a constituent unit (III) derived from an unsaturated monocarboxylic acid ester monomer (c),

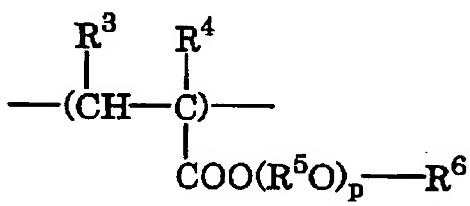
wherein the constituent units (I') and (III) each accounts for not less than 1% by mass relative to all constituent units but the constituent unit (I') accounts for not more than 50 mole percent relative to all constituent units.

7) The cement admixture according to 6),

wherein the number of milliequivalents of carboxyl groups contained in each gram of the polymer (G) as determined on the unneutralized basis is 0 to 0.8 meq/g.

8) The cement admixture according to 6) or 7),

wherein the polymer (B5) is a polymer comprising, as essential constituent units, a constituent unit (IV) derived from a (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d) represented by the general formula (3):



(3)

wherein R^3 and R^4 are the same or different and each represents a hydrogen atom or a methyl group, the p R^5O groups are the same or different and each R^5O represent an oxyalkylene group containing 2 to 18 carbon atoms, p is a mean addition number of moles of the oxyalkylene group and

represents a number of 1 to 500 and R^6 represents a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms,

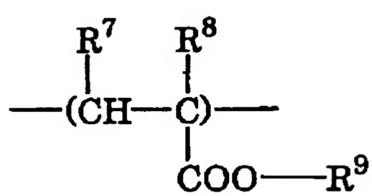
and a constituent unit (II)derived from an unsaturated monocarboxylic acid monomer (b).

9) The cement admixture according to 6) or 7),

wherein the polymer (B5) is a polymer comprising, as essential constituent units, the constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the general formula (2) and a constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e).

10) The cement admixture according to any of 6) to 9),

wherein the constituent unit (III) derived from an unsaturated monocarboxylic acid ester monomer (c) is a constituent unit (IV) derived from a (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d) or a constituent unit (VI) derived from a hydrophobic unsaturated monocarboxylic acid ester monomer (f) represented by the general formula (4):



(4)

wherein R^7 and R^8 are the same or different and each represents a hydrogen atom or a methyl group and R^9 represents a hydrocarbon group containing 1 to 30 carbon atoms.

11) The cement admixture according to any 1) to 10) comprising

a non-polymerizable (poly)alkylene glycol (P) not

containing an alkenyl group.

12) The cement admixture according to 1) comprising the unsaturated (poly)alkylene glycol ether monomer (a1).

13) The cement admixture according to any of 2) to 11) comprising the unsaturated (poly)alkylene glycol ether monomer (a2).

14) A cement composition comprising, as essential constituents, the cement admixture according to any of 1) to 13), cement and water.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The cement admixtures according to the present invention comprise respectively, as essential constituents, the two kinds of polymer, (1) polymer (A1) and polymer (B1), (2) polymer (A2) and polymer (B2), (3) polymer (A3) and polymer (B3), (4) polymer (A3) and polymer (B4), or (5) polymer (G) and polymer (B5). In this description, these cement admixtures are represented by the following words, namely cement admixture (1), cement admixture (2), cement admixture (3), cement admixture (4) and cement admixture (5), respectively. The cement admixture (1) can be obtained by mixing together the two polymers (A1) and (B1) separately synthesized. The cement admixture (2) can be obtained by mixing together the two polymers (A2) and (B2) separately synthesized. The cement admixture (3) can be obtained by mixing together the two polymers (A3) and (B3) separately synthesized. The cement admixture (4) can be obtained by mixing together the two polymers (A3) and (B4) separately synthesized. The cement admixture (5) can be obtained by mixing together the two polymers (G) and (B5) separately synthesized.

These polymers are respectively described below.

The polymer (A1), (A2), and (A3) of the present

invention, are polymers comprising, as essential constituent units, an unsaturated (poly)alkylene glycol ether monomer-derived constituent unit and an unsaturated monocarboxylic acid monomer-derived constituent unit. Further, in this description, polymer (A) means all of the polymer (A1), (A2), and (A3).

The polymer (A1) is a polymer comprising, as essential constituent units, the constituent unit (I) derived from an unsaturated (poly)alkylene glycol ether monomer (a1) represented by the above general formula (1) and the constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b). Although the polymer (A1) is a polymer comprising the constituent units (I) and (II) as essential constituents, it may further contain another or other copolymerizable monomer-derived constituent units. These constituent units in polymer (A1) each may comprise one single species or two or more species.

It is necessary that, in the above the polymer (A1), the constituent units (I) and (II) each account for at least 1% by mass relative to all constituent units and the proportion of the constituent unit (I) be not more than 50 mole percent relative to all constituent units. When the proportion of constituent unit (I) is less than 1% by mass, the content of the unsaturated (poly)alkylene glycol ether monomer (a)-derived oxyalkylene group in the polymer (A1) is too low and, when the proportion of constituent unit (II) is less than 1% by mass, the content of the unsaturated monocarboxylic acid monomer (b)-derived carboxyl group in the polymer (A1) is too low, so that, in either case, no sufficient dispersing ability can be exhibited. On the other hand, for obtaining the polymer (A1) with high dispersing ability in high yields, it is important that the proportion of the constituent unit (I) should be not more than 50 mole percent relative to all constituent units, since the polymerizability of the

unsaturated (poly)alkylene glycol ether monomer (a1) is low. While it is necessary that the proportion of the constituent unit (I) be at least 1% by mass relative to 100% by mass of all constituent units, the proportion is preferably not less than 5% by mass, more preferably not less than 10% by mass, still more preferably not less than 20% by mass, most preferably not less than 40% by mass. The total content (% by mass) of the constituent units (I) and (II) in the polymer (A1) is preferably 50 to 100% by mass, more preferably 70 to 100% by mass, relative to the whole polymer (A1).

While it is necessary that, in the above polymer (A1), the carboxyl group-containing constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b) accounts for at least 1% by mass relative to all constituent units, it is preferred that the number of milliequivalents of carboxyl groups contained in each gram of polymer (A1) as determined on the unneutralized basis be 0.2 to 5.0 meq/g. It is thus preferred that the proportion of each constituent unit constituting the polymer (A1) be selected so that the number of milliequivalents of carboxyl groups in the polymer (A1) amount to a value within the above range. The number of milliequivalents of carboxyl groups is more preferably 0.3 to 4.5 meq/g, still more preferably 0.3 to 4.0 meq/g, in particular 0.4 to 3.5 meq/g, most preferably 0.4 to 3.0 meq/g. The upper limit to the content of constituent unit (II) can be selected in a manner such that the number of milliequivalents of carboxyl groups contained in the polymer (A1) as determined on the unneutralized basis may be within the above range.

The term "number of milliequivalents of carboxyl groups contained in each gram of polymer (A1) (meq/g) as determined on the unneutralized basis" is used herein to include the case where the polymer (A1) is in a salt form. The methods of calculation are shown below for the case

where it occurs as an acid and for the case where it occurs as a salt. While, in the following calculations, the constituent unit (II)-derived carboxyl groups alone are exemplified, another carboxyl group-containing constituent unit, for example the constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e), which is to be mentioned later herein, if contained in the polymer, this must be taken into consideration in calculating the number of milliequivalents of carboxyl groups.

(Calculation Example 1): When a copolymer with a monomer (a1)/monomer (b) content ratio of 90/10 (% by mass) is obtained by using acrylic acid as monomer (b), the number of milliequivalents of monomer (b)-derived carboxyl groups per gram of the above polymer as determined on the unneutralized basis is $(0.1/72) \times 1{,}000 = 1.39$ (meq/g), since the molecular weight of acrylic acid is 72.

(Calculation Example 2): When a copolymer with a monomer (a1)/monomer (b) content ratio of 80/20 (% by mass) is obtained by using sodium acrylate as monomer (b), the number of milliequivalents of monomer (b)-derived carboxyl groups per gram of the above polymer as determined on the unneutralized basis is $(0.2 \times 72/94)/(0.8 + 0.2 \times 72/94)/72 \times 1{,}000 = 2.23$ (meq/g), since the molecular weight of sodium acrylate is 94 and that of acrylic acid is 72. When acrylic acid is used in carrying out polymerization and, after polymerization, the acrylic acid-derived carboxylic groups are completely neutralized with sodium hydroxide, the same result as in this calculation example is obtained.

In addition to the monomer-based method of calculating the number of milliequivalents of carboxyl groups contained in each gram of polymer (A1) (meq/g) as determined on the unneutralized basis, as mentioned above, the number can also be calculated by measuring the acid value of the above polymer while taking into consideration

the counter ion species relative to the carboxyl groups in the polymer.

As the above polymer (A1), the polymer (C) may also be used, which comprises, as essential constituent units, the constituent unit (I) derived from an unsaturated (poly)alkylene glycol ether monomer (a1) represented by the above general formula (1), the constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b) and the constituent unit (III) derived from an unsaturated monocarboxylic acid ester monomer (c). The cement admixture in which the above polymer (A1) is such polymer (C) is one of the preferred embodiments of the present invention. While the polymer (C) is a polymer comprising the constituent units (I), (II) and (III) as essential constituent units, it may further comprise another or other copolymerizable monomers-derived other constituent units. These constituent units of the polymer (C) each may comprise one single species or two or more species.

Referring to the above polymer (C), it is necessary that the constituent units (I), (II) and (III) each accounts for not less than 1% by mass relative to all constituent units and that the sum of the proportions of the constituent units (II) and (III) is greater than the proportion of the constituent unit (I) on the mole ratio basis. When the proportion of constituent unit (I) is less than 1% by mass, the content of an unsaturated (poly)alkylene glycol ether monomer (a1)-derived oxyalkylene groups in the polymer (C) is too low. When the proportion of constituent unit (II) is less than 1% by mass, the content of an unsaturated monocarboxylic acid monomer (b)-derived carboxyl groups in the polymer (C) is too low and, when the proportion of constituent unit (III) is less than 1% by mass, the content of the unsaturated monocarboxylic acid ester monomer (c)-derived substituents in the polymer (C) is too low. In each case, any

satisfactory level of dispersing ability cannot be attained. As for the mutual proportions of the constituent units, it is necessary, for obtaining the polymer (C) with high dispersing ability in high yields, that the sum of the proportions of the constituent units (II) and (III) is greater than the proportion of the constituent unit (I) on the mole ratio basis, since the unsaturated (poly)alkylene glycol ether monomer (a1) is low in polymerizability. The proportion of constituent unit (I) relative to 100% by mass of all constituent units is required to be not less than 1% by mass and is preferably not less than 5% by mass, more preferably not less than 10% by mass, still more preferably not less than 20% by mass, most preferably not less than 40% by mass. The proportion of constituent (III) relative to 100% by mass of all constituent units is required to be not less than 1% by mass and is preferably not less than 2% by mass, more preferably not less than 3% by mass, still more preferably not less than 4% by mass, most preferably not less than 5% by mass. The total content (% by mass) of the constituents (I), (II) and (III) in the polymer (C) is preferably 50 to 100% by mass, more preferably 70 to 100% by mass, relative to the polymer (C) as a whole.

In the above polymer (C), like in the polymer (A1), it is necessary that the constituent unit (II) containing the unsaturated monocarboxylic acid monomer (b)-derived carboxyl group account for at least 1% by mass relative to all constituent units and, further, it is preferred that the number of milliequivalents of carboxyl groups contained in each gram of polymer (C) as determined on the unneutralized basis be 0.2 to 5.0 meq/g, hence it is preferred that the content ratios of the polymer (C)-constituting constituent units be selected so that the number of milliequivalents of carboxyl groups in the polymer (C) may fall within the above range. For attaining a high level of dispersion-retaining ability, in particular,

it is more preferable that the above-mentioned number of milliequivalents of carboxyl groups be 0.2 to 2.0 meq/g, still more preferably 0.2 to 1.5 meq/g, in particular 0.2 to 1.0 meq/g, most preferably 0.2 to 0.8 meq/g. The upper limit to the content of constituent unit (II) can be selected so that the number of milliequivalents of carboxyl groups contained in the polymer (C) as determined on the unneutralized basis may be within the above range. The number of milliequivalents of carboxyl groups per gram of polymer (C) can be calculated in the same manner as mentioned above referring to the polymer (A1).

Since the polymer (A1) and polymer (C) may contain another carboxyl-containing constituent unit, for example the above-mentioned constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e), in addition to the carboxyl-containing constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b), the number of milliequivalents of carboxyl groups (meq/g) contained in the polymer (A1) and polymer (C) is not limited to the case where it originates in the constituent unit (II) alone.

The above polymer (A1) can be produced by copolymerizing a monomer component comprising, as essential constituents, an unsaturated (poly)alkylene glycol ether monomer (a1), which provides the constituent unit (I), and an unsaturated monocarboxylic acid monomer (b), which provides the constituent unit (II). The method of production thereof is not limited to this method but may comprise, for example, using a monomer before alkylene oxide addition, namely methallyl alcohol or a like unsaturated alcohol, in lieu of monomer (a1), copolymerizing the same with a monomer (b) in the presence of a polymerization initiator (where necessary, copolymerizing these monomers with a further monomer(s) copolymerizable therewith) and, thereafter, causing 1 to 500 moles, on average, of an alkylene oxide to add to the

resulting copolymer. In the same manner, the polymer (C) can be produced by copolymerizing a monomer component comprising, as essential constituents, an unsaturated (poly)alkylene glycol ether monomer (a1), which provides the constituent unit (I), an unsaturated monocarboxylic acid monomer (b), which provides the constituent unit (II), and an unsaturated monocarboxylic acid ester monomer (c), which provides the constituent unit (III). The method of production is not limited to this but may comprise copolymerizing a monomer component prior to, or without, alkylene oxide addition and, thereafter, causing an alkylene oxide to add to the resulting copolymer.

The above-mentioned polymer (A2) is a polymer comprising, as essential constituent units, the constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the above general formula (2), the constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b) and the constituent unit (III) derived from an unsaturated monocarboxylic ester monomer (c), wherein the constituent units (I'), (II) and (III) each accounts for not less than 1% by mass relative to all constituent units but the constituent unit (I') accounts for not more than 50 mole percent relative to all constituent units and the sum of the proportions of the constituent units (II) and (III) is greater than the proportion of the constituent unit (I') on the mole ratio basis. This polymer (A2) is the above polymer (C), wherein the constituent unit (I) derived from an unsaturated (poly)alkylene glycol ether monomer (a1) in the polymer (C) is the constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2).

The number of milliequivalents of carboxyl groups contained in each gram of polymer (A2) (meq/g) as determined on the unneutralized basis and the preferred range thereof are the same as described for the polymer (C).

Further, in the preferred embodiment of the polymer (A2), the R^2 of the unsaturated (poly)alkylene glycol ether monomer (a2) is a hydrogen atom. Namely, the polymer (A2) is preferably the polymer (C).

The above-mentioned polymer (A3) is a polymer comprising, as essential constituent units, the constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the above general formula (2) and the constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b), wherein the constituent units (I') and (II) each accounts for not less than 1% by mass relative to all constituent units but the constituent unit (I') accounts for not more than 50 mole percent relative to all constituent units. This polymer (A3) is the above polymer (A1), wherein the constituent unit (I) derived from an unsaturated (poly)alkylene glycol ether monomer (a1) in the polymer (A1) is the constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2).

The number of milliequivalents of carboxyl groups contained in each gram of polymer (A3) (meq/g) as determined on the unneutralized basis and the preferred range thereof are the same as described for the polymer (A1). Further, in the preferred embodiment of the polymer (A3), the polymer (A3) is preferably the polymer (A2), and more preferably the polymer (C), wherein the R^2 of the unsaturated (poly)alkylene glycol ether monomer (a2) is a hydrogen atom.

The above-mentioned polymer (G) is a polymer comprising, as essential constituent units, the constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the above general formula (2) and the constituent unit (III) derived from an unsaturated monocarboxylic acid ester monomer (c).

In the above polymer (G), it is necessary that the

constituent units (I′) and (III) each account for at least 1% by mass relative to all constituent units and that the constituent unit (I′) account for not more than 50 mole percent relative to all constituent units. When the proportion of the constituent unit (I′) is less than 1% by mass, the unsaturated (poly)alkylene glycol ether monomer (a2)-derived oxyalkylene group content in the polymer (G) is too low and, when the proportion of the constituent unit (III) is less than 1% by mass, the unsaturated monocarboxylic acid ester monomer (c)-derived carboxylic acid ester content in the polymer (G) is too low, so that the polymer cannot produce any sufficient dispersion retaining ability. On the other hand, since the unsaturated (poly)alkylene glycol ether monomer (a2) is low in polymerizability, it is important, for obtaining the polymer (G) with high dispersion retaining ability in high yields, that the proportion of constituent unit (I′) be not more than 50 mole percent relative to all constituent units. While the proportion of constituent unit (I′) is required to be not less than 1% by mass relative to all constituent units, the proportion is preferably not less than 5% by mass, more preferably not less than 10% by mass, still more preferably not less than 20% by mass, in particular not less than 40% by mass. The proportion of constituent unit (III) is required to be not less than 1% by mass relative to all constituent units but is preferably not less than 2% by mass, more preferably not less than 5% by mass, still more preferably not less than 10% by mass, in particular not less than 20% by mass. The total content (% by mass) of the constituent units (I′) and (III) in the polymer (G) is preferably 50 to 100% by mass, more preferably 70 to 100% by mass, of the polymer (G) as a whole.

The above polymer (G) is a polymer comprising the constituent units (I′) and (III) as essential constituent units, and may comprise a further copolymerizable monomer-

derived constituent unit or units. These constituent units in the polymer (G) each may comprise one single species or two or more species. Therefore, the polymer (G) may comprise a carboxyl group-containing constituent unit in addition to the constituent units (I') and (III). The carboxyl group-containing constituent unit may be the constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b), the constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e) or another carboxyl group-containing constituent unit.

In the practice of the present invention, it is preferred that the number of milliequivalents of carboxyl groups contained in each gram of the above polymer (G) as determined on the unneutralized basis be 0 to 0.8 meq/g, hence it is preferred that the content ratios of the polymer (G)-constituting constituent units be selected so that the number of milliequivalents of carboxyl groups in the polymer (G) may fall within such range. For attaining a high level of dispersion retaining ability, in particular, it is more preferable that the above-mentioned number of milliequivalents of carboxyl groups be 0 to 0.7 meq/g, still more preferably 0 to 0.6 meq/g, further more preferably 0 to 0.5 meq/g, in particular 0 to 0.4 meq/g, most preferably 0 to 0.2 meq/g.

The above-mentioned "number of milliequivalents of carboxyl groups contained in each gram of polymer (G) (meq/g) as determined on the unneutralized basis" is intended to include the case where the polymer (G) is in a salt form, like in the case of polymer (A1), and the methods of calculation for the acid form and salt form are the same as mentioned above for the polymer (A1). The polymer (G) may comprise, as the carboxyl group-containing constituent unit, any of the constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b), the constituent unit (V) derived from an unsaturated

dicarboxylic cid monomer (e) and other carboxyl group-containing constituent units, and all carboxyl groups are to be taken into consideration in calculating the number of milliequivalents of carboxyl groups. The number of milliequivalents of carboxyl groups per gram of the above polymer (meq/g) as determined on the unneutralized basis can be determined not only by the above-mentioned monomer-based methods of calculation but also by measuring the acid value of the polymer while taking into consideration the kind of counter ion to the carboxyl groups in the polymer.

The above polymer (G) can be produced by copolymerizing a monomer composition comprising, as essential constituents, an unsaturated (poly)alkylene glycol ether monomer (a2), which provides the constituent unit (I'), and an unsaturated monocarboxylic acid ester monomer (c), which provides the constituent unit (III). The method of production thereof is not limited to such method but may comprise, for example, using a monomer before alkylene oxide addition, namely methallyl alcohol or a like unsaturated alcohol, in lieu of the monomer (a2), copolymerizing the same with a monomer (c) in the presence of a polymerization initiator (where necessary, copolymerizing these monomers with a further monomer(s) copolymerizable therewith) and, thereafter, causing 1 to 500 moles, on average, of an alkylene oxide to add to the resulting copolymer.

Referring to the general formulas (1) and (2) given hereinabove, the number of carbon atoms in R^1 in the oxyalkylene group R^1O is suitably 2 to 18 but preferably 2 to 8, more preferably 2 to 4. In the case of alkylene oxide adducts derived from two or more species optionally selected from among ethylene oxide, propylene oxide, butylene oxide, styrene oxide and the like, the mode of addition may be of the random, block and/or alternating type, for instance. For securing a balance between the

hydrophilicity and hydrophobicity, it is preferred that the oxyalkylene group comprises the oxyethylene group as an essential constituent, with the oxyethylene group preferably accounting for at least 50 mole percent, more preferably at least 90 mole percent.

In the above general formulas (1) and (2), the mean addition numbers m and n of moles of oxyalkylene group(s) are appropriately 1 to 500. When these mean addition numbers of moles decrease, the hydrophilicity of the polymer obtained tends to decrease, hence the dispersing ability tends to decrease. When they exceed 500, the copolymerizability tends to decrease. Preferably, they are not less than 2, more preferably not less than 5, still more preferably not less than 10, in particular not less than 15, most preferably not less than 20. Preferably, they are not more than 300. The preferred range may be, for example, 2 to 500, 5 to 500, 10 to 500, 15 to 500, or 20 to 300.

In the above general formula (2), R^2 may be either a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms. The hydrocarbon group containing 1 to 30 carbon atoms is preferably a hydrocarbon group not having a radical-polymerizable unsaturated bond and is suitably an alkyl group (aliphatic alkyl group or alicyclic alkyl group) containing 1 to 30 carbon atoms or a benzene ring-containing aromatic group containing 6 to 30 carbon atoms such as a phenyl group, an alkylphenyl group, a phenylalkyl group, an (alkyl)phenyl-substituted phenyl group or a naphthyl group. With the increase in the number of carbon atoms in the hydrocarbon group, the hydrophobicity increases and the dispersing ability decreases. Therefore, the number of carbon atoms in R^2 when this is a hydrocarbon group is preferably 1 to 22, more preferably 1 to 18, still more preferably 1 to 12, in particular 1 to 4. The case where R^2 is a hydrogen atom is most preferred.

In the above general formulas (1) and (2), the number of carbon atoms in the alkenyl group represented by Y is appropriately 2 to 8, preferably not less than 3 but not more than 5. Suitable as the alkenyl group containing 2 to 8 carbon atoms are vinyl, allyl, methallyl, 3-butenyl, 3-methyl-3-butenyl, 3-methyl-2-butenyl, 2-methyl-3-butenyl, 2-methyl-2-butenyl and 1,1-dimethyl-2-propenyl. Among them, allyl, methallyl and 3-methyl-3-butenyl are preferred.

The unsaturated (poly)alkylene glycol ether monomer (a1) represented by the above general formula (1) and the unsaturated (poly)alkylene glycol ether monomer (a2) represented by the above general formula (2), can be produced by various methods but the typical methods are described in the following.

1) When the unsaturated (poly)alkylene glycol ether monomer (a1), and R^2 is a hydrogen atom in the general formula (2), the monomers (a1) and (a2) can be produced by causing 1 to 500 moles of at least one alkylene oxide containing 2 to 18 carbon atoms to add to an unsaturated alcohol having an alkenyl group containing 3 to 8 carbon atoms such as allyl alcohol, methallyl alcohol, 3-methyl-3-buten-1-ol, 3-methyl-2-buten-1-ol or 2-methyl-2-buten-1-ol, in the presence of an alkaline catalyst such as potassium hydroxide or sodium hydroxide, or acid catalyst such as boron trifluoride or tin tetrachloride.

2) When R^2 is a hydrocarbon group containing 1 to 30 carbon atoms in the above general formula (2), the monomers can be obtained by reacting a halogenated hydrocarbon containing 1 to 30 carbon atoms such as methyl chloride with the resulting compound obtained by adding 1 to 500 moles of at least one alkylene oxide containing 2 to 18 carbon atoms to an unsaturated alcohol in the above method, in the presence of an alkaline catalyst such as sodium hydroxide.

3) When R^2 is a hydrocarbon group containing 1 to 30

carbon atoms in the above general formula (2), the monomers can be obtained by reacting a halogenated alkenyl containing 3 to 8 carbon atoms such as allyl chloride or methallyl chloride with the resulting compound obtained by adding 1 to 500 moles of at least one alkylene oxide containing 2 to 18 carbon atoms to an alcohol or phenol containing 1 to 30 carbon atoms such as methanol or phenol, in the presence of an alkaline catalyst such as sodium hydroxide, in the different method from the method mentioned in the above 2).

In the production methods 1) and 2), when a compound containing an active hydrogen such as a saturated alcohol other than the above-mentioned unsaturated alcohol (for example, methanol or ethanol) or water exists in the reaction system on the occasion of adding an alkylene oxide to the unsaturated alcohol, a composition which contains a (poly)alkylene glycol not containing a radical-polymerizable substituent, namely a non-polymerizable (poly)alkylene glycol (P) not containing an alkenyl group as a byproduct, can be obtained by using the above active hydrogen as a starting material, in addition to the main products unsaturated (poly)alkylene glycol ether monomer (a1) and (a2). On the other hand, in the production method 3), since an unreacted alkylene oxide adducts with a halogenated alkenyl corresponds to a non-polymerizable (poly)alkylene glycol (P) not containing an alkenyl group, a composition which contains (poly)alkylene glycol (P) as a byproduct can be obtained. A cement admixture comprising a polymer obtained by copolymerization of a monomer composition containing the unsaturated (poly)alkylene glycol ether monomer (a1) or (a2) produced by the above-mentioned production method 1), 2), or 3), is one preferred mode in the practice of the present invention. Although the (poly)alkylene glycol (P) obtained as a byproduct contains at least one terminal hydrogen atom,

when the (poly)alkylene glycol (P) is a (poly)alkylene glycol containing hydrogen atoms at both terminals, for example, (poly)ethylene glycol or (poly)ethylene(poly)propylene glycol, the molecular weight of the (poly)alkylene glycol (P) obtained by using water containing two active hydrogen as a starting material is higher than that of unsaturated (poly)alkylene glycol ether monomer (a1) or (a2) obtained by using an unsaturated alcohol containing one active hydrogen as a starting material. In this case, the molecular weight of the (poly)alkylene glycol (P) is same or twice level of that of unsaturated (poly)alkylene glycol ether monomer (a1) or (a2).

Suited for use as the above unsaturated (poly)alkylene glycol ether monomer (a1) are (poly)ethylene glycol allyl ether, (poly)ethylene glycol methallyl ether, (poly)ethylene glycol 3-methyl-3-butenyl ether, (poly)ethylene(poly)propylene glycol allyl ether, (poly)ethylene(poly)propylene glycol methallyl ether, (poly)ethylene(poly)propylene glycol 3-methyl-3-butenyl ether, (poly)ethylene(poly)butylene glycol allyl ether, (poly)ethylene(poly)butylene glycol methallyl ether and (poly)ethylene(poly)butylene glycol 3-methyl-3-butenyl ether. In the practice of the present invention, one or more of these can be used as monomer(s) (a1) for providing the constituent unit (I).

Suited for use as the above unsaturated (poly)alkylene glycol ether monomer (a2) are methoxy(poly)ethylene glycol allyl ether, methoxy(poly)ethylene glycol methallyl ether, methoxy(poly)ethylene glycol 3-methyl-3-butenyl ether, methoxy(poly)ethylene(poly)propylene glycol allyl ether, methoxy(poly)ethylene(poly)propylene glycol methallyl ether, methoxy(poly)ethylene(poly)propylene glycol 3-methyl-3-butenyl ether, methoxy(poly)ethylene(poly)butylene glycol

allyl ether, methoxy(poly)ethylene(poly)butylene glycol methallyl ether and methoxy(poly)ethylene(poly)butylene glycol 3-methyl-3-butenyl ether, in addition to the compounds mentioned above for the unsaturated (poly)alkylene glycol ether monomer (a1) represented by the general formula (1). In the practice of the present invention, one or more of these can be used as monomer(s) (a2) for providing the constituent unit (I').

In the case of the cement admixture (1) comprising the polymer (A1) and polymer (B1) as essential constituents of the invention, two or more monomers (a1) differing in the mean addition number m of moles of an oxyalkylene group can be used in combination as the unsaturated (poly)alkylene glycol ether monomer (a1) represented by the general formula (1). Suitable are combinations of two monomers (a1) differing in m by not less than 10 (preferably differing in m by not less than 20) and combinations of three or more monomers (a1) differing in the mean addition number m of moles by not less than 10 (preferably differing in m by not less than 20) from one another. As regards the ranges of m's to be combined, the combination of a monomer (a1) whose mean addition number m of moles is 40 to 500 and a monomer (a1) whose m is 1 to 40 (with the difference in m being not less than 10, preferably not less than 20) and the combination of a monomer (a1) whose mean addition number m of moles is 20 to 500 and a monomer (a1) whose m is 1 o 20 (with the difference in m being not less than 10, preferably not less than 20) are appropriate. It is possible to use a combination of two or more monomers (a1) differing in the mean addition number m of moles of an oxyalkylene group(s) in each of the polymers (A1) and (C) or to use the above monomers differing in the mean addition number m of moles of an oxyalkylene group(s) from one polymer to another.

In the case of the cement admixtures (2) to (5) ofthe

present invention comprising respectively, as essential constituents, the two kinds of polymer, (2) polymer (A2) and polymer (B2), (3) polymer (A3) and polymer (B3), (4) polymer (A3) and polymer (B4), or (5) polymer (G) and polymer (B5), two or more monomers (a2) differing in the mean addition number n of moles of an oxyalkylene group can be used in combination as the unsaturated (poly)alkylene glycol ether monomer (a2) represented by the general formula (2). Suitable are combinations of two monomers (a2) differing in n by not less than 10 (preferably differing in n by not less than 20) and combinations of three or more monomers (a2) differing in the mean addition number n of by not less than 10 (preferably differing in n by not less than 20) from one another. As regards the ranges of n's to be combined, the same ranges as mentioned above for m in the case of the cement admixture (1) are appropriate. It is possible to use a combination of two or more monomers (a2) differing in the mean addition number n of moles of an oxyalkylene group(s) in each of the polymers (A2), (A3) and (G) or to use the above monomers differing in the mean addition number n of moles of an oxyalkylene group(s) from one polymer to another.

Preferred as the unsaturated monocarboxylic acid monomer (b), which provides the constituent unit (II), are (meth)acrylic acid monomers. Thus preferred are acrylic acid, methacrylic acid and crotonic acid, and monovalent metal salts, divalent metal salts, ammonium salts and organic amine salts of these. From the copolymerizability viewpoint, however, (meth)acrylic acid and salts thereof are more preferred. Two or more of these monomers (b) may be used in combination. In the polymers (A1), (C), (A2), (A3), and (G), however, it is preferred that the monomer (b) used to provide the constituent unit (II) comprise acrylic acid or a salt thereof as an essential constituent.

The unsaturated monocarboxylic acid ester monomer (c)

used to provide the constituent unit (III) is an esterification product derived from an unsaturated monocarboxylic acid and a monohydric alcohol, preferably an esterification product derived from a (meth)acrylic acid monomer, namely acrylic acid, methacrylic acid or crotonic acid, used as the unsaturated monocarboxylic acid, and a monohydric alcohol. More specifically, the (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d) capable of providing the constituent unit (IV) represented by the above general formula (3) or a hydrophobic unsaturated monocarboxylic acid ester monomer (f) capable of providing the constituent unit (VI) represented by the general formula (4) is preferred as the unsaturated monocarboxylic acid ester monomer (c). The monomer (c) providing the constituent unit (III) may comprise one single species or two or more of such species as mentioned above.

In the polymer (G), in particular, the constituent unit (III) derived from an unsaturated monocarboxylic acid ester monomer (c) preferably comprises an acrylic acid ester monomer-derived constituent unit as an essential constituent unit. Thus, the unsaturated monocarboxylic acid ester monomer (c), which provides the constituent unit (III), preferably comprises, as an essential constituent, an esterification product derived from acrylic acid and a monohydric alcohol. More specifically, it is preferred that the constituent unit (IV) represented by the above general formula (3) comprise, as an essential constituent unit, a (poly)alkylene glycol monoacrylic acid ester monomer-derived constituent unit (corresponding to the case where, in the above general formula (3), R^3 and R^4 each is a hydrogen atom) or the constituent unit (VI) represented by the above general formula (4) comprise a hydrophobic acrylic acid ester monomer-derived constituent unit (corresponding to the case where, in the above general formula (4), R^7 and R^8 each is a hydrogen atom) as an

essential constituent unit.

When the (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d), which provides the constituent unit (IV) represented by the above general formula (3), is used as the unsaturated monocarboxylic acid ester monomer (c), which provides the constituent unit (III), the number of carbon atoms contained in the oxyalkylene group R^5O in the above general formula (3) is appropriately 2 to 18 but preferably 2 to 8, more preferably 2 to 4. In the case of adducts of two or more alkylene oxides arbitrarily selected from among ethylene oxide, propylene oxide, butylene oxide, styrene oxide and the like, the mode of addition may be any of the random, block, alternating or other addition types. In the above general formula (3), the mean addition number n of moles of an oxyalkylene group(s) is appropriately 1 to 500 but is preferably 1 to 300, more preferably 1 to 200, still more preferably 1 to 100, in particular 1 to 50. As this mean addition number of moles increases, the copolymerizability with the unsaturated (poly)alkylene glycol ether monomer (a1) which provides the constituent unit (I) or the unsaturated (poly)alkylene glycol ether monomer (a2) which provides the constituent unit (I'), tends to decrease. Furthermore, in the above general formula (3), R^6 may be a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms. Appropriate as the hydrocarbon group containing 1 to 30 carbon atoms are those specifically mentioned hereinabove referring to R^2. Since, however, the hydrophobicity increases and the dispersing ability decreases as the increase in the number of carbon atoms in the hydrocarbon group, the number of carbon atoms in the hydrocarbon group represented by R^6 is preferably 1 to 22, more preferably 1 to 18, still more preferably 1 to 12, in particular 1 to 5.

When the (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d), which provides the constituent unit (IV)

represented by the above general formula (3), is used as the unsaturated monocarboxylic acid ester monomer (c) to provide the constituent unit (III), the following are suited for use as the monomer (d): hydroxyalkyl (meth)acrylates (corresponding to the case where, in the above general formula (3), p is 1 and R^6 is a hydrogen atom) such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and hydroxybutyl (meth)acrylate; various polyalkylene glycol mono(meth)acrylates (corresponding to the case where, in the above general formula (3), p is not less than 2 and R^6 is a hydrogen atom) such as polyethylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate and polybutylene glycol mono(meth)acrylate; various alkoxy(poly)alkylene glycol mono(meth)acrylates such as methoxy(poly)ethylene glycol mono(meth)acrylate and methoxy(poly)ethylene(poly)propylene glycol mono(meth)acrylate; and the like.

When the (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d) is used, the polymer (G), in particular, preferably comprises a (poly)alkylene glycol monoacrylic acid ester monomer-derived constituent unit as an essential constituent unit. Suitable as the monomer which provides such constituent unit are hydroxyalkyl acrylates (corresponding to the case where, in the above general formula (3), p is 1 and R^3, R^4 and R^6 each is a hydrogen atom) such as 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate and 2-hydroxybutyl acrylate; various polyalkylene glycol monoacrylates (corresponding to the case where, in the above general formula (3), p is not less than 2 and R^3, R^4 and R^6 each is a hydrogen atom) such as polyethylene glycol monoacrylate, polypropylene glycol monoacrylate and polybutylene glycol monoacrylate; and various alkoxy(poly)alkylene glycol monoacrylates (corresponding to the case where, in the above general formula (3), R^3 and R^4 each is a hydrogen atom and R^6 is a hydrocarbon group

containing 1 to 30 carbon atoms) such as methoxy(poly)ethylene glycol monoacrylate and methoxy(poly)ethylene(poly)propylene glycol monoacrylate.

When the hydrophobic unsaturated monocarboxylic acid ester monomer (f), which provides the constituent unit (VI) represented by the above general formula (4), is used as the unsaturated monocarboxylic acid ester monomer (c) to provide the constituent unit (III), R^9 in the general formula (4) may be a hydrocarbon group containing 1 to 30 carbon atoms. Suitable as the hydrocarbon group containing 1 to 30 carbon atoms are those specifically mentioned above referring to R^2. Since, however, the hydrophobicity increases and the dispersing ability decreases as the increase in the number of carbon atoms in the hydrocarbon group, the number of carbon atoms in the hydrocarbon group represented by R^9 is preferably 1 to 22, more preferably 1 to 18, still more preferably 1 to 12, most preferably 1 to 4.

When the hydrophobic unsaturated monocarboxylic acid ester monomer (f), which provides the constituent unit (VI) represented by the above general formula (4), is used as the unsaturated monocarboxylic acid ester monomer (c) to provide the constituent unit (III)), the followings are suited for use as the monomer (f): alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, octyl (meth)acrylate and cyclohexyl (meth)acrylate; and aromatic (meth)acrylates such as phenoxy (meth)acrylate and benzyl (meth)acrylate.

Referring to the polymer (G), in particular, when the hydrophobic unsaturated monocarboxylic acid ester monomer (f) is used, it is preferred that a constituent unit derived from a hydrophobic acrylic acid ester monomer as an essential constituent unit is comprised. Referring to a monomer, which provides the above constituent unit, alkyl acrylates corresponding to the case where R^7 and R^8 in the

general formula (4) are hydrogen atoms and R^9 is an alkyl group containing 1 to 30 carbon atoms, more preferably 1 to 22 carbon atoms, still more preferably 1 to 18 carbon atoms, in particular 1 to 12 carbon atoms, most preferably 1 to 4 carbon atoms, are preferred. Suited for use as the above alkyl acrylates are methyl acrylate, ethyl acrylate, propyl acrylate and butyl acrylate.

In producing the above polymers (A1), (C), (A2), (A3), and (G), an unsaturated dicarboxylic acid monomer (e) which provides the constituent unit (V) and/or a monomer (g) which provides the constituent unit (VII) can be used in addition to the monomers providing the essential constituent units.

Suitable as the unsaturated dicarboxylic acid monomer (e), which provides the constituent unit (V) are maleic acid, citraconic acid, fumaric acid, and metal salts, ammonium salts and amine salts of these and, further, maleic anhydride and citraconic anhydride as the anhydrides thereof. Among them, maleic acid or a salt thereof and maleic anhydride are preferred. These monomers (e) may be used singly or two or more may be used in combination.

The monomer (g), which provides the above-mentioned constituent unit (VII), is a monomer other than the monomers (a1) to (f) but copolymerizable with the other monomers. Suitable as such monomer (g) are half esters and diesters derived from unsaturated dicarboxylic acid monomers, such as maleic acid, maleic anhydride, fumaric acid, itaconic acid and citraconic acid, and alcohols containing 1 to 30 carbon atoms; half amides and diamides derived from the above-mentioned unsaturated dicarboxylic acid monomers and amines containing 1 to 30 carbon atoms; half esters and diesters derived from the above-mentioned unsaturated dicarboxylic acid monomers and alkyl(poly)alkylene glycols, which are adducts of 1 to 500 moles of an alkylene oxide(s) containing 2 to 18 carbon

atoms with the above-mentioned alcohols or amines; half esters and diesters derived from the above-mentioned unsaturated dicarboxylic acid monomers and glycols containing 2 to 18 carbon atoms or polyalkylene glycols, which are adducts of 2 to 500 moles of an alkylene oxide(s) with such glycols; half amides derived from maleamidic acid and glycols containing 2 to 18 carbon atoms or polyalkylene glycols, which are adducts of 2 to 500 moles of an alkylene oxide(s) with such glycols; (poly)alkylene glycol di(meth)acrylates such as triethylene glycol di(meth)acrylate, (poly)ethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylate and (poly)ethylene glycol-(poly)propylene glycol di(meth)acrylate; multifunctional (meth)acrylates such as hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate and trimethylolpropane di(meth)acrylate; (poly)alkylene glycol dimaleates such as triethylene glycol dimaleate and polyethylene glycol dimaleate; unsaturated sulfonic acids and monovalent metal salts, divalent metal salts, ammonium salts and organic amine salts thereof, for example vinylsulfonates, (meth)allylsulfonates, 2-(meth)acryloxyethylsulfonates, 3-(meth)acryloxypropylsulfonates, 3-(meth)acryloxy-2-hydroxypropylsulfonates, 3-(meth)acryloxy-2-hydroxypropyl sulfophenyl ether, 3-(meth)acryloxy-2-hydroxypropyloxysulfobenzoates, 4-(meth)acryloxybutylsufonates, (meth)acrylamidomethylsulfonates, (meth)acrylamidoethylsulfonates, 2-methylpropanesulfonic acid (meth)acrylamide, and styrenesulfonic acid; amides derived from unsaturated monocarboxylic acids and amines containing 1 to 30 carbon atoms, for example methyl(meth)acrylamide; vinyl aromatics such as styrene, α-methylstyrene, vinyltoluene and p-methylstyrene; alkanediol mono(meth)acrylates such as 1,4-

butanediolmono(meth)acrylate, 1,5-pentanediol mono(meth)acrylate and 1,6-hexanediol mono(meth)acrylate; dienes such as butadiene, isoprene, 2-methyl-1,3-butadiene and 2-chloro-1,3-butadiene; unsaturated amides such as (meth)acrylamide, (meth)acrylalkylamides, N-methylol(meth)acrylamide and N,N-dimethyl(meth)acrylamide; unsaturated cyano compounds such as (meth)acrylonitrile and α-chloroacrylonitrile; unsaturated esters such as vinyl acetate and vinyl propionate; unsaturated amines such as aminoethyl (meth)acrylate, methylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, dibutylaminoethyl (meth)acrylate and vinylpyridine; divinyl aromatics such as divinylbenzene; cyanurates such as triallyl cyanurate; and siloxane derivatives such as polydimethylsiloxanepropylaminomaleamidic acid, polydimethylsiloxaneaminopropyleneaminomaleamidic acid, polydimethylsiloxane-bis(propylaminomaleamidic acid), polydimethylsiloxane-bis(dipropyleneaminomaleamidic acid), polydimethylsiloxane-(1-propyl-3-acrylate), polydimethylsiloxane-(1-propyl-3-methacrylate), polydimethylsiloxane-bis(1-propyl-3-acrylate) and polydimethylsiloxane-bis(1-propyl-3-methacrylate). These may be used singly or two or more of them may be used combinedly.

The above polymers (B1), (B2), (B3), (B4) and (B5) are oxyalkylene group- or polyoxyalkylene group- and carboxyl group-containing polymers. These may be used singly or two or more of them may be used combinedly. Further, in this description, polymer (B) means all of the polymer (B1), (B2), (B3), (B4) and (B5).

The above polymer (B) is a polymer other than the corresponding polymer (A) and polymer (G) in the cement admixture. Namely, the polymer (B1) is a polymer other than the polymer (A1) in the cement admixture (1), the

polymer (B2) is a polymer other than the polymer (A2) in the cement admixture (2), the polymer (B3) is a polymer other than the polymer (A3) in the cement admixture (3), the polymer (B4) is a polymer other than the polymer (A3) in the cement admixture (4), and the polymer (B5) is a polymer other than the polymer (G) in the cement admixture (5).

Suitable as the oxyalkylene or polyoxyalkylene group, which is an essential structural element of the polymer (B), are oxyalkylene groups containing 2 to 18 carbon atoms, or polyoxyalkylene groups, which are adducts of one or more of such oxyalkylene groups with a mean addition number of moles thereof exceeding 1, preferably not less than 2, more preferably not less than 5, still more preferably not less than 10. Referring to the above (poly)oxyalkylene groups, the number of carbon atoms in the oxyalkylene group is suitably 2 to 18, preferably 2 to 8, more preferably 2 to 4. As for the alkylene oxide adducts derived from two or more alkylene oxides arbitrarily selected from among ethylene oxide, propylene oxide, butylene oxide and styrene oxide, among others, the mode of addition may be of any type, random, block or alternating, for instance. Preferably, however, the oxyalkylene groups comprise an oxyethylene group(s) as essential constituent(s) and, more preferably, oxyethylene groups account for not less than 50 mole percent thereof.

Suitable as the polymers (B1), (B2) and (B5) in the above polymer (B) are polymers (A) (polymers (A1), (A2) and (A3) such as the above-mentioned polymer (C)) or (G) other than the polymer (A) or (G) to be combined, a polymer (polymer (B3)) comprising, as essential constituent units, the constituent unit (IV) derived from (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d) represented by the above general formula (3) and the constituent unit (II)derived from an unsaturated monocarboxylic acid monomer

(b), a polymer (polymer (B4)) comprising, as essential constituent units, the constituent unit (I′) derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the above general formula (2) and the constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e), and hydrophilic graft polymers derived from polyether compounds and unsaturated carboxylic acid monomers by graft polymerization, as described in Japanese Kokai Publication Hei-07-53645, Japanese Kokai Publication Hei-08-208769 and Japanese Kokai Publication H0ei-8-208770. Among them, the polymer (B3) or (B4) is preferably used. Thus, in preferred embodiments, the polymer (B) is one of the above-mentioned polymers (B3) and (B4). The polymers (B3) and polymers (B4) may be used singly or two or more of them may be used in combination.

The cement admixtures (1) to (4) according to the present invention comprise at least one polymer (A) and at least one polymer (B), respectively. The combination of polymer (A) and polymer (B) includes the case (1) in which the polymer (A) is combined with the polymer (B) which is other than the polymer (A) and/or the case (2) in which the polymer (A) is combined with the polymer (B) which is another polymer (A) (polymer (A′)). In case (1), such cement admixture comprises, as polymer (B), a polymer other than the polymer (A), namely such a polymer (B3) or polymer (B4) as mentioned above and, in case (2), it comprises two or more polymers (A), at least one of which serves as polymer (A) and in which at least one polymer (polymer (A′)) other than the polymer (A) serves as polymer (B). The two or more polymers in case (2) are preferably two or more polymers (A) differing in acid value, molecular weight, constituent unit structure and/or constituent unit composition, for instance. In the cement admixture (1), suitable as the combination of two or more polymers differing in constituent unit structure is the combination

of polymers differing in the mean addition number m of moles of an oxyalkylene group(s) of the unsaturated (poly)alkylene glycol ether monomer (a1) represented by the general formula (1). In the cement admixtures (2), (3), and (4), suitable as the combination of two or more polymers differing in constituent unit structure is the combination of polymers differing in the mean addition number n of moles of an oxyalkylene group(s) of the unsaturated (poly)alkylene glycol ether monomer (a2) represented by the general formula (2).

In another preferred specific combination of polymer (A1) and polymer (B1) in the cement admixture (1) according to the present invention, the above-mentioned polymer (C) is used as polymer (A1) and a polymer (A) (polymer (A1), (A2) or (A3)), other than the polymer (C), is used as polymer (B1). Further preferred combinations are as follows: combination of polymer (A1) and, as polymer (B1), a polymer (A) (polymer (A1), (A2) or (A3)) differing in constituent unit(s) from the polymer (A1); combination of polymer (A1) and, as polymer (B1), a polymer (A) identical in constituent units to but differing in constituent unit content ratio from the polymer (A1); combination of the above-mentioned polymer(C) as polymer (A1) and, as polymer (B1), a polymer (A) (polymer (A1), (A2) or (A3)) differing in constituent unit(s) from the polymer (C); combination of the above-mentioned polymer (C) as polymer (A1) and, as polymer (B1), a polymer (A1) identical in constituent units to but differing in constituent unit content ratio from the polymer (C); and so forth. Preferred among others, however, is the combined use of two or more polymers differing in the mean addition number m of moles of the oxyalkylene group(s) in the unsaturated (poly)alkylene glycol ether monomer (a1) presented by the above general formula (1), which provides an essential constituent unit in the polymer (A1) or (C).

In another preferred specific combination of polymer (A2) and (B2) in the cement admixture (2) according to the present invention, the above-mentioned polymer (C) is used as polymer (A2) and a polymer (A) (polymer (A1), (A2) or (A3)), other than the polymer (C), is used as polymer (B2). Further preferred combinations are as follows: combination of polymer (A2) and, as polymer (B2), a polymer (A) (polymer (A1), (A2) or (A3)) differing in constituent unit(s) from the polymer (A2); combination of polymer (A2) and, as polymer (B2), a polymer (A) identical in constituent units to but differing in constituent unit content ratio from the polymer (A2); combination of the above-mentioned polymer(C) as polymer (A2) and, as polymer (B2), a polymer (A) (polymer (A1), (A2) or (A3)) differing in constituent unit(s) from the polymer (C); combination of the above-mentioned polymer (C) as polymer (A2) and, as polymer (B2), a polymer (A2) identical in constituent units to but differing in constituent unit content ratio from the polymer (C); and so forth. Preferred among others, however, is the combined use of two or more polymers differing in the addition number n of moles of the oxyalkylene group(s) in the unsaturated (poly)alkylene glycol ether monomer (a2) presented by the above general formula (2), which provides an essential constituent unit in the polymer (A2) or polymer (C).

In the cement admixture (5) according to the present invention, preferred combinations of the polymer (G) and (B5) are as follows: combination of the polymer (G) and, as polymer (B5), a polymer (G) differing in constituent unit(s) from the polymer (G); combination of polymer (G) and, as polymer (B5), a polymer (G) identical in constituent units to but differing in constituent unit content ratio from the polymer (G); combination of polymer (G) and, as polymer (B5), a polymer (A) (a polymer (A1), (A2) or (A3)) other than the polymer (G)

The above polymer (B3) is a polymer comprising, as essential constituent units, the constituent unit (IV) derived from (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d) represented by the above general formula (3) and the constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b). It may further comprise another or other copolymerizable monomer-derived constituent unit or units. Each of these constituent units in the polymer (B3) may comprise one single species or two or more species.

The ratio between the constituent unit (IV) and constituent unit (II) (constituent unit (IV)/constituent unit (II); % by mass) in the above polymer (B3) is preferably 1 to 99/99 to 1. The total content (% by mass) of the constituent unit (IV) and constituent unit (II) in the polymer (B3) is preferably 50 to 100% by mass, more preferably 70 to 100% by mass, based on the whole polymer (B3). The upper limit to the content of the constituent unit (II) can be placed at a level such that the number of milliequivalents of carboxyl groups contained in the polymer (B3) as determined on the unneutralized basis falls within the range to be mentioned later herein.

Further, for attaining a high level of dispersing ability, the number of milliequivalents of carboxyl groups contained in each gram of polymer (B3) as determined on the unneutralized basis is preferably 0.3 to 3.5 meq/g, and the proportions of the constituent units constituting the polymer (B3) are preferably selected so that the number of milliequivalents of carboxyl groups in the polymer (B3) may fall within such range. The number of milliequivalents of carboxyl groups is more preferably 0.3 to 3.0 meq/g, still more preferably 0.4 to 2.5 meq/g. The polymer (B3) may contain, in addition to the carboxyl group-containing constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b), a further carboxyl group-

containing constituent unit such as the above-mentioned constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e), hence the number of milliequivalents of carboxyl groups contained in the polymer (B3) is not always limited to that owing to the constituent unit (II).

The above-mentioned "number of milliequivalents of carboxyl groups contained in each gram of polymer (B3) (meq/g) as determined on the unneutralized basis" is intended to include the case where the polymer (B3) is in a salt form, and the methods of calculation for the acid form and salt form are the same as mentioned above for the polymer (A1). When the polymer (B3) comprises a further carboxyl-containing constituent unit (e.g. the constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e)) other than the constituent unit (II), the number of milliequivalents of carboxyl groups as resulting from such further unit should be included in the calculation. The number of milliequivalents of carboxyl groups per gram of the polymer (B3) (meq/g) as determined on the unneutralized basis can be determined not only by the above-mentioned monomer-based methods of calculation but also by measuring the acid value of the polymer while taking into consideration the kind of counter ion to the carboxyl groups in the polymer.

The above polymer (B3) can be produced, for example, by copolymerizing a monomer component comprising, as essential constituents, a (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d), which provides the constituent unit (IV), and an unsaturated monocarboxylic acid monomer (b), which provides the constituent unit (II). The method of production thereof is not limited to such method but may comprise, for example, directly esterifying at least part of the carboxyl groups of a polymer obtained by polymerizing a monomer component

containing a (meth)acrylic acid monomer, namely acrylic acid, methacrylic acid or crotonic acid, as an essential constituent, with an alkoxypolyalkylene glycol having a hydrocarbon group containing 1 to 30 carbon atoms at one terminal.

When, in producing the above polymer (B3), a (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d), which provides the constituent unit (IV), represented by the above general formula (3) is used, the number of carbon atoms in the oxyalkylene group R^5O is suitably 2 to 18 but preferably 2 to 8, more preferably 2 to 4, in the above general formula (3). In the case of alkylene oxide adducts derived from two or more species optionally selected from among ethylene oxide, propylene oxide, butylene oxide, styrene oxide and the like, the mode of addition may be of the random, block and/or alternating type, for instance. For securing a balance between the hydrophilicity and hydrophobicity, it is preferred that the oxyalkylene group comprises the oxyethylene group as an essential constituent, with the oxyethylene group preferably accounting for at least 50 mole percent, more preferably at least 90 mole percent. In the above general formula (3), the mean addition number n of moles of oxyalkylene group(s) is appropriately 1 to 500 but preferably is 2 to 500, more preferably 5 to 500, still more preferably 10 to 500, in particular 15 to 500, most preferably 20 to 300. When this mean addition number of moles decreases, the hydrophilicity of the polymer obtained tends to decrease, hence the dispersing ability tends to decrease. When it exceeds 500, the copolymerizability tends to decrease. Further, in the above general formula (3), R^6 may be either a hydrogen atom or a hydrocarbon group containing 1 to 30 carbon atoms but preferably is a hydrocarbon group containing 1 to 30 carbon atoms. Suitable as the hydrocarbon group containing 1 to 30 carbon

atoms are those specifically mentioned hereinabove referring to R^2. With the increase in the number of carbon atoms in the hydrocarbon group, the hydrophobicity increases and the dispersing ability decreases. Therefore, the number of carbon atoms in R^6 when this is a hydrocarbon group is preferably 1 to 22, more preferably 1 to 18, still more preferably 1 to 12, in particular 1 to 5.

When a (poly)alkylene glycol mono(meth)acrylic acid ester monomer (d), which provides the constituent unit (IV) represented by the above general formula (3), is used in producing the above polymer (B3), the monomer (d) includes, among others, (meth)acrylic acid- or crotonic acid-C_{2-18} alkylene oxide adducts; esterification products derived from (meth)acrylic acid or crotonic acid on one hand and, on the other, alkoxypolyalkylene glycols obtained by addition of an alkylene oxide(s) containing 2 to 18 carbons atoms to any of saturated aliphatic alcohols containing 1 to 30 carbon atoms, such as methanol, ethanol, 2-propanol, 1-butanol, 1-pentanol, 1-hexanol, octanol, 2-ethyl-1-hexanol, nonyl alcohol, lauryl alcohol, cetyl alcohol and stearyl alcohol, unsaturated aliphatic alcohols containing 3 to 30 carbon atoms, such as crotyl alcohol and oleyl alcohol, alicyclic alcohols containing 3 to 30 carbon atoms, such as cyclohexanol, and aromatic alcohols containing 6 to 30 carbon atoms, such as phenol, phenylmethanol (benzyl alcohol), methylphenol (cresol), dimethylphenol (xylenol) and nonylphenol. As specific examples of the monomer (d), there may be mentioned the same monomers as mentioned above referring to the case where the monomer (d), which provides the constituent unit (IV), represented by the above general formula (3) is used as the unsaturated monocarboxylic acid ester monomer (c) to provide the constituent unit (III) in the polymer (C). The monomer (d), which provides the constituent unit (IV), to be used in producing the polymer (B3) may comprise one single species or a combination of

two or more species.

The unsaturated monocarboxylic acid monomer (b), which provides the constituent unit (II), to be used in producing the polymer (B3) is preferably a (meth)acrylic acid monomer. Preferred species are acrylic acid, methacrylic acid, crotonic acid, and monovalent metal salt, divalent metal salts, ammonium salts, and organic amine salts thereof. From the copolymerizability viewpoint, however, (meth)acrylic acid and salts thereof are more preferred. The monomer (b) may comprise one single species or a combination of two or more species.

In addition to the monomer constituents providing the essential constituent units, any of an unsaturated dicarboxylic acid monomer (e), which provides the constituent unit (V), a hydrophobic unsaturated monocarboxylic acid ester monomer (f), which provides the constituent unit (VI), and a monomer (g), which provides the constituent unit (VII), may be used as another copolymerizable monomer in producing the polymer (B3). Preferred species of such monomers are those already mentioned hereinabove.

The above-mentioned polymer (B4) is a polymer comprising, as essential constituent units, the constituent unit (I') derived from an unsaturated (poly)alkylene glycol ether monomer (a2) represented by the above general formula (2) and the constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e). It may further comprise another or other copolymerizable monomer-derived constituent unit or units. These constituent units in the polymer (B4) each may comprise one single species or two or more species.

In the above polymer (B4), the constituent unit (I') and constituent unit (V) each accounts for at least 1% by mass of all constituent units, and the proportion of the constituent unit (I') is preferably not more than 50 mole

percent of all constituent units. When the proportion of the constituent unit (I') is less than 1% by mass, the content, in the polymer (B4), of the unsaturated (poly)alkylene glycol ether monomer (a2)-derived oxyalkylene group(s) is too low. When the proportion of the constituent unit (V) is less than 1% by mass, the content, in the polymer (B4), of the unsaturated dicarboxylic acid monomer (e)-derived carboxyl groups is too low. In either case, the dispersing ability tends to decrease. Further, since the unsaturated (poly)alkylene glycol ether monomer (a2) is low in polymerizability, it is preferred that the proportion of the constituent unit (I') be not more than 50 mole percent of all constituent units so that the polymer (B4) can be obtained with high dispersing ability and in high yields. The total content (% by mass), in the polymer (B4), of the constituent units (I') and (V) is preferably 50 to 100% by mass, more preferably 70 to 100% by mass, on the whole polymer (B4) basis.

Further, for attaining a high level of dispersing ability, the number of milliequivalents of carboxyl groups contained in each gram of the polymer (B4) as determined on the unneutralized basis is preferably 0.3 to 3.5 meq/g, and the proportions of the constituent units constituting the polymer (B4) are preferably selected so that the number of milliequivalents of carboxyl groups in the polymer (B4) may fall within such range. The number of milliequivalents of carboxyl groups is more preferably 0.3 to 3.0 meq/g, still more preferably 0.4 to 2.5 meq/g. The upper limit to the content of the constituent unit (V) can be placed at a level such that the number of milliequivalents of carboxyl groups contained in the polymer (B4) as determined on the unneutralized basis is within the above range.

The above-mentioned "number of milliequivalents of carboxyl groups contained in each gram of polymer (B4)

(meq/g) as determined on the unneutralized basis" is intended to include the case where the polymer (B4) is in a salt form, and the methods of calculation for the acid form and salt form are the same as mentioned above for the polymer (A1). The polymer (B4) may contain, in addition to the constituent unit (V) derived from an unsaturated dicarboxylic acid monomer (e), a further carboxyl-containing constituent unit such as the above-mentioned constituent unit (II) derived from an unsaturated monocarboxylic acid monomer (b), hence the number of milliequivalents of carboxyl groups contained in the polymer (B4) is not always limited to that owing to the constituent unit (V). The number of milliequivalents of carboxyl groups per gram of the polymer (B4) (meq/g) as determined on the unneutralized basis can be determined not only by the above-mentioned monomer-based methods of calculation but also by measuring the acid value of the polymer while taking into consideration the kind of counter ion to the carboxyl groups in the polymer.

The above polymer (B4) can be produced, for example, by copolymerizing a monomer component comprising, as essential constituents, an unsaturated (poly)alkylene glycol ether monomer (a2), which provides the constituent unit (I'), and an unsaturated dicarboxylic acid monomer (e), which provides the constituent unit (V). The method of production thereof is not limited to such method but may comprise, for example, using a monomer before alkylene oxide addition, namely methallyl alcohol or a like unsaturated alcohol, in lieu of the monomer (a2), copolymerizing the same with a monomer (e) in the presence of a polymerization initiator (where necessary copolymerizing these monomers with a further monomer(s) copolymerizable therewith) and, thereafter, causing 1 to 500 moles, on average, of an alkylene oxide to add to the resulting copolymer.

As for the details and specific examples of the polymer (B4)-constituting constituent units and the monomers which provide the constituent units, the corresponding descriptions given hereinabove referring to the polymer (A1) or (A2) are to be referred to.

The above polymers (A), (B) and (G), can be produced by polymerizing monomer compositions comprising the monomers mentioned above, using a polymerization initiator. The polymerization can be carried out in the manner of solution polymerization or bulk polymerization, for instance.

The solution polymerization can be carried out either batchwise or continuously. Suited for use as the solvent on that occasion are water; lower alcohols such as methyl alcohol, ethyl alcohol and isopropyl alcohol; aromatic or aliphatic hydrocarbons such as benzene, toluene, xylene, cyclohexane and n-hexane; ester compounds such as ethyl acetate; and ketone compounds such as acetone and methyl ethyl ketone. These may be used singly or two or more of them may be used in combination. In view of the solubilities of the starting monomers and the polymers (A), (B) and (G) and the convenience in using the polymers, at least one solvent selected from the group consisting of water and lower alcohols containing 1 to 4 carbon atoms is preferably used. In that case, methyl alcohol, ethyl alcohol and isopropyl alcohol are particularly effective among lower alcohols containing 1 to 4 carbon atoms.

In carrying out the polymerization in aqueous solution, use is made, as a radical polymerization initiator, a water-soluble polymerization initiator, for example, a persulfate salt such as ammonium persulfate, sodium persulfate or potassium persulfate; hydrogen peroxide; or a water-soluble azo initiator, for example an azoamidine compound such as 2,2'-azobis-2-methylpropionamidine hydrochloride, a cyclic azoamidine

compound such as 2,2'-azobis-2-(2-imidazolin-2-yl)propane hydrochloride, or an azonitrile compound such as 2-carbamoylazoisobutyronitrile and, on that occasion, an accelerator may be used combinedly, for example an alkali metal sulfite such as sodium hydrogen sulfite, a metabisulfite, sodium hypophosphate, an Fe(II) salt such as Mohr's salt, sodium hydroxymethanesulfinate dihydrate, hydroxylamine hydrochloride, thiourea, L-ascorbic acid (salt) or erythorbic acid (salt). When hydrogen peroxide is used as the water-soluble polymerization initiator, such an accelerator as L-ascorbic acid (salt) is preferably used in combination.

In carrying out the polymerization using a lower alcohol, aromatic hydrocarbon, aliphatic hydrocarbon, ester compound or ketone compound as the solvent, a peroxide such as benzoyl peroxide or lauroyl peroxide; a hydroperoxide such as cumene hydroperoxide; or such an azo compound as azobisisobutyronitrile, for instance, is used as the polymerization initiator. On that occasion, an accelerator such as an amine compound may be used in combination. Further, when a mixed solvent composed of water and a lower alcohol is used, an appropriate polymerization initiators or polymerization initiator-accelerator combination can be selected from among the above-mentioned various initiators or initiator-accelerator combinations. The polymerization temperature may appropriately be selected depending on the solvent and polymerization initiator employed. Generally, the polymerization is carried out at 0 to 120°C.

The above-mentioned bulk polymerization is carried out at a temperature of 50 to 200°C using, as the polymerization initiator, peroxide such as benzoyl peroxide or lauroyl peroxide; a hydroperoxide such as cumene hydroperoxide; or an azo compound such as azobisisobutyronitrile, for instance.

An injection method of each monomer to a reaction

vessel is not particularly restricted but includes a method comprising injecting the whole monomers to a reaction vessel collectively at the initial stage, a method comprising injecting the whole monomers to a reaction vessel divisionally or continuously, and a method comprising injecting part of monomers to a reaction vessel at the initial stage and then injecting the remnant to a reaction vessel divisionally or continuously. Specifically, there may be mentioned the following methods (1) to (4).

(1) A method comprising injecting the whole monomers to a reaction vessel continuously.

(2) A method comprising injecting the whole monomer (a1) or (a2) to a reaction vessel collectively at the initial stage, and then injecting the other monomers to a reaction vessel continuously.

(3) A method comprising injecting part of monomer (a1) or (a2) to a reaction vessel at the initial stage and then injecting the remnant of monomer (a1) or (a2) and the other monomers to a reaction vessel continuously.

(4) A method comprising injecting part of monomer (a1) or (a2) and part of the other monomers to a reaction vessel at the initial stage, and then injecting the remnant of monomer (a1) or (a2) and the remnant of the other monomers to a reaction vessel in several portions, respectively by turns.

Further, by varying the injection speed of each monomer to a reaction vessel continuously or gradationally and changing the mass ratio of each injected monomer per time continuously or gradationally, a copolymer mixture containing each constituent unit differing in the content in the copolymer may be synthesized in the polymerization reaction system. In addition, a radical polymerization initiator may be placed in a reaction vessel at the initial stage, or may be added dropwise to a reaction vessel, and these methods may be used combinedly according to need.

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP02/05144

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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